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16. ABSTRACT

In this study galvanized steel panels were exposed for 6 months using an automatic covering device at a materials exposure site located at RTP, NC. Galvanized steel panels were boldly exposed to wet and dry deposition. Another set of panels were mounted on a motor-driven rack that moved the panels under a shelter, thereby preventing rain from falling on them. These panels were sprayed with deionized water during each rain event. IC and AA analysis of the runoff from panels indicated that wet deposition enhances the dissolution rate of Zn surface. Much of the Zn dissolved under both clean rain and dry deposition and total deposition conditions can be accounted for by dry and wet deposition of sulfur species and their reactions of Zn compounds that form on the passive protective film on the galvanized steel panels.

This information is essential to the development of a damage model that partitions the effects of wet and dry deposition on galvanized steel.

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INTRODUCTION

Galvanizing steel is a well-known technique for protecting iron from corrosion. Studies show that galvanized steel, which consists of a zinc coating bonded strongly to a steel substrate, reacts with air pollutants that deposit on the surfaces by wet and dry deposition (1-11). Since its use is widespread, damage to galvanized steel, resulting in significant economic losses, could be occurring in many areas in the United States. To address this issue, the National Acid Precipitation Assessment Program has developed a research program whose ultimate goal is the development of damage functions that can be used to estimate the economic savings associated with a given control strategy.

A damage function is a mathematical relationship that expresses the extent of damage, for instance, the amount of corrosion of a metal, as a function of environmental conditions. Damage to galvanized steel is measured as the weight loss of zinc per unit area or, equivalently, as the loss in thickness. To determine the extent of damage taking place under ambient conditions, the compounds that deposit onto a surface must be identified and their amounts of deposition determined. The extent of corrosion can be calculated if the amount of Zn corroded per amount of compound deposited is known.

Recently, we have conducted a series of short-term laboratory exposure experiments to identify the compounds that enhance the corrosion rate of galvanized steel above that expected under clean ambient conditions (12,13). In the absence of air pollutants other than CO_2, it is believed that Zn will corrode by the following electrochemical half reactions:

$$Zn + H_2O \rightarrow Zn(OH)_2 + 2H^+ + 2e^-$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

The reactions result in the formation of a protective layer that consists of $Zn(OH)_2$ and/or basic zinc carbonates that form when $Zn(OH)_2$ reacts with dissolved CO_2. Laboratory studies suggest that these compounds can react with active ions in precipitation and with ions produced by deposition of SO_2, HCHO, and HNO_3, and their subsequent reactions in the presence of moisture, in particular, dew (12,13). The reaction products are, in general, water soluble, and can be removed from the surface by precipitation. To determine whether these processes take place under ambient conditions, field exposure experiments must be conducted.

In the past, galvanized steel field exposure studies have been conducted by exposing test panels for a number of years and measuring their weight loss at fixed intervals of time. In general, little effort was made to characterize the environmental exposure conditions. The field sites were classified according to whether they were marine, rural, or industrial sites. More recently, a series of

field studies have begun in which the air quality parameters SO_2, O_3, NO_X, and particulate concentrations; the rain chemistry parameters – amount, pH, Cl^-, NO_3^-, $SO_4^=$; and meteorological variables, such as temperature, relative humidity, windspeed, and wind direction, are measured (6). The objective of these field studies is to generate a data base that can be used to perform a multivariate regression analysis to determine the impact of environmental parameters on the atmospheric corrosion rate of galvanized steel.

While such an approach will generate much useful information, it is unlikely that it can be used to generate a damage function because, although such an approach can be used to measure the correlation between certain input variables and the output variable (the weight loss per unit area), the establishment of such correlations does not imply a cause and effect relationship between the variables. Therefore, we believe that the field data can best be used to determine whether the data is consistent with the predictions of models generated from laboratory data that are generated under carefully controlled conditions. To reduce the correlations that are expected to exist between important field environmental variables, we have designed and conducted a controlled field study in which test panels are exposed under the following conditions: (1) total exposure (dry and wet deposition); (2) dry deposition only; and (3) dry deposition and clean wet deposition. The field site is located at Research Triangle Park, NC, a relatively clean site. Rain and rain runoff samples were collected for each of 44 rain events that occurred between January 28, 1986, and September 9, 1986, and were analyzed for Zn, Cl^-, NO_3^-, and $SO_4^=$. A preliminary analysis of the runoff data is presented.

Experimental

A computer-controlled covering/spray system was designed, constructed, and installed on the campus of Research Triangle Institute in Research Triangle Park, NC. The system consists of a set of exposure racks, a shelter, a control and data acquisition system, precipitation sensing instrumentation, and a deionized (DI) water spray system. The rack system, constructed of aluminum, contains a stationary set of racks and a mobile set of racks mounted on a moveable frame connected to the drive chain of a garage door motor. The racks are designed so that up to 144 4- by 6-in. test panels can be mounted on each rack. The panels are mounted at 30° to the horizontal and are held in place by ceramic insulators. Rain runoff collectors are located at some of the test positions and consist of PVC troughs connected to 1-L polyethylene collection bottles. The collector system is designed so that the moisture deposited onto a test panel will drain into the trough and subsequently be collected in the polyethylene bottles.

The control and data acquisition system consists of a computer (Radio Shack TRS-80 Model 4) and an interface device. The interface device is a card cage system that contains a real-time clock, a 24-bit I/O control board, a 16-channel A/D board, two rain counter boards, a 2-channel D/A board,

and a personality module. The precipitation sensor is an Aerochem Metrics rain sensor. A Weather Measurement Corporation tipping bucket rain gauge is used to detect precipitation in increments of 0.01 in. The DI spray system is located inside the shelter and consists of a 2000-L holding tank for water, a pump, a carbon adsorber tank, two mixed-bed ion exchange resin tanks, a 0.2-μM particle filter, four PVC valves that are controlled by the computer system, and 24 spray nozzles.

In the presence of moisture, the precipitation sensor sends a signal to the computer that subsequently turns on the rack motor. The moveable sample racks are then moved under the shelter. The amount of rain is measured using the tipping bucket and the output of the bucket is monitored by the computer. The computer receives a pulse from the bucket system each time 0.01 in. of precipitation has accumulated. After 0.03 in. of rain has accumulated, the computer turns on the DI spray system and DI water is sprayed for ~30 s, the time required to deliver approximately 0.03 in. to the inside panels. Analysis of the clean rain spray shows that the uptake of CO_2 by the spray droplets is sufficiently fast so that the pH of the spray is 5.6. The spray procedure is repeated each time 0.03 in. of precipitation accumulates in the tipping bucket. The mobile rack system remains inside the shelter as long as the precipitation sensor is wet. Once it dries, the computer turns on the garage door motor and the racks are returned to the boldly exposed positions.

After each rain event, runoff samples are collected from a galvanized steel test panel that is boldly exposed and from one that is exposed under dry deposition plus clean wet deposition conditions. Both types of samples are analyzed for Cl^-, NO_3^-, and $SO_4^=$ by ion chromatography and for Zn using atomic absorption spectroscopy. In addition, the pH and amount of the rain and rain runoff samples are measured. Procedures for conducting the chemical analyses have been published elsewhere (12,13).

The data presented here were collected during 44 rain events between January 28, 1986, and September 9, 1986, at the Reseach Triangle Park site.

Results and Discussion

Figures 1 and 2 show the accumulated depositions of Cl^-, NO_3^-, $SO_4^=$, and Zn for the clean rain plus dry deposition and total deposition conditions, respectively. Depositions were calculated for each rain event using the following relationship:

$$D(X) = \frac{[X]V}{A},$$

where

[X] = concentration of X in the runoff in nanomoles/milliliter,
V = volume of runoff in milliliters,
A = area of one side of test panel (155 cm^2), and
D(X) = deposition of X in nanomoles/square centimeter.

The average flux for each compound is shown in Table 1. The deposition obtained under the clean wet plus dry deposition condition represents the actual dry deposition of the compound if the deposited species forms a compound that is soluble in the pH 5.6 spray. The total deposition contains contributions from compounds that are soluble in ambient rain. The Zn deposition is the amount of Zn dissolved per unit area.

Significant amounts of Cl^-, NO_3^-, and $SO_4^=$ were dry deposited onto the test panel. The ratio of $SO_4^=$ to NO_3^- dry deposition was 3.4, and the Cl^- dry deposition was 69% of that found for NO_3^-. $SO_4^=$ deposition consisted of both the dry depositions of particulate $SO_4^=$ and gaseous SO_2 that reacted on the Zn surface to produce $SO_4^=$. The NO_3^- found in the clean rain runoff most likely arose from the dry deposition of HNO_3 and particulate nitrate. The ratio of $SO_4^=$ to NO_3^- for total deposition was 2.6 and the Cl^- to NO_3^- ratio was 0.43. The ratio of dry deposition to total deposition was 0.75, 0.46, and 0.69 for Cl^-, NO_3^-, and $SO_4^=$, respectively, and shows that both dry and wet deposition contributed substantially to the total deposition.

The difference between the amounts of Zn dissolved under the two exposure conditions (F[clean rain plus dry deposition] = 5.93 nmol/cm^2 · day and F[total deposition] = 8.55 nmol/cm^2 · day) demonstrates that ambient wet deposition enhanced the dissolution rate of Zn and suggests that the enhancement was caused by impurities in the precipitation. To further investigate the relationships between dry and wet deposition of air and precipitation impurities and the Zn dissolution rate, a statistical analysis of the data was conducted to (1) determine the correlations that exist between the Zn dissolved and the anions found in the clean and ambient rain runoffs and (2) compare these correlations with those obtained from laboratory studies. This preliminary evaluation focused on the role of $SO_4^=$ and NO_3^- in the production of soluble Zn corrosion products.

The data were evaluated using a two-parameter linear regression model in which the depositions of $SO_4^=$ and NO_3^- were the input variables and the deposition of Zn was the output variable, i.e.,

$$z = \alpha x + \beta y + \phi,$$

where

$z = D(Zn)$,
$x = D(SO_4^=)$, and
$y = D(NO_3^-)$.

α and β are the regression coefficients for x and y, respectively, and ϕ is the intercept. The correlations between the output and input variables, as well as the averages and standard deviations of the variables for the clean rain plus dry deposition and total deposition exposure conditions, are shown in Table 2. All data collected during the field study were included in the analysis.

For both exposure conditions, the average and the standard deviation for $SO_4^=$ were significantly larger than that found for NO_3^-. A strong correlation was found between NO_3^- and $SO_4^=$ under the total deposition exposure conditions, i.e., $r(x,y) = 0.813$, that resulted from the high correlations between the variables in the incident precipitation. The clean rain plus dry deposition correlation coefficient between the same variables was 0.472. The rather large values for the coefficients show that x and y were not independent and, in some sense, the environmental and meteorological conditions produced a poor statistical design for the field experiment.

The results of the two-parameter regression analyses are shown in Table 3. The 90% confidence marginal intervals based on the t distribution for α are 1.13 ± 0.12 and 0.88 ± 0.15 for clean rain plus dry deposition and total deposition, respectively. The former value is consistent with laboratory studies that showed a 1:1 relationship between SO_2 deposited and Zn dissolved in dew. The total deposition α interval is also consistent with a 1:1 relationship between $SO_4^=$ and Zn; however, since rain pH is strongly correlated with rain anion concentration, the correlation found cannot be used to determine whether the controlling factor in the dissolution of Zn by precipitation is $[H^+]$ or $[SO_4^=]$. The 90% confidence marginal intervals for the NO_3^- coefficient β are 0.20 ± 0.42 for clean rain plus dry deposition and 0.56 ± 0.40 for total deposition. Included in the dry deposition interval are both 0.5, the result expected from laboratory studies, and 0 where deposition of NO_3^- has no effect on the dissolution rate of Zn. The total deposition β coefficient interval contains the laboratory value but not 0. The lack of definitive information generated for β is caused by the structure of the field study data set. Not only are variations of $SO_4^=$ depositions substantially greater than those of NO_3^-, but, in addition, the variables are highly correlated. Both of these results lead to a lack of precision in the estimate of β.

The values for the intercepts ϕ and the standard errors show that under both exposure conditions the intercepts do not differ significantly from 0. The results of these analyses show that most of the variation in the dissolution of Zn can be accounted for by the deposition of S compounds. A closer examination of the two-parameter regression results shows that 90.1% of the variation in Zn dissolution under clean rain plus dry deposition conditions can be accounted for by variations in the dry deposition of $SO_4^=$, whereas under total deposition conditions, variations in the $SO_4^=$ depositions account for 75.6% of the variation. These results suggest that a one-parameter model that contains only the $SO_4^=$ contributions should yield a reasonable good fit to the data. The results of the one-parameter model are shown in Table 4 and shows that the introdution of NO_3^- into the model does not significantly improve the quality of the fit.

In addition to the enhancement in corrosion caused by NO_3^- and $SO_4^=$, it has been suggested that the dry depositions of HCHO and Cl-containing compounds and clean rain itself can contribute to the production of soluble Zn corrosion products on galvanized steel (12,13). To a certain degree,

the difference between the amount of Zn dissolved under clean rain plus dry deposition and total deposition exposure conditions gives a direct estimate of the impact of clean rain. The result that the amount of Zn dissolved under total deposition conditions is 44% higher than that obtained from clean rain suggests that the clean contribution is small compared with that caused by rain impurities. This point is further substantiated by the result that much of the dissolved Zn obtained under clean rain plus dry deposition conditions can be accounted for by the dry deposition of $SO_4^=$ and NO_3^-. The assumed contribution to corrosion due to clean rain is based on the result that $Zn(OH)_2$ and $ZnCO_3$ are slightly soluble in H_2O. The literature value for $ZnCO_3$ solubility is ~80 nmol/ml (14). However, to contribute to corrosion under ambient conditions, the time scale of the dissolution process must be on the order of or shorter than the residence time of a rain droplet on the surface. This result is important in interpreting the dissolution of Zn under clean rain plus dry deposition conditions. The DI spray system delivers deionized water to the surfaces in units of 0.03 in., and it takes approximately 30 s to deliver this amount of spray. Therefore, the residence time of a spray droplet may differ substantially from that of the ambient rain. Thus, the lack of evidence for a clean rain effect could be explained by the artificially short surface residence times of the droplets generated by the DI spray system.

To address the impact of clean rain more adequately, the regression analysis should be expanded to include the amount of rain as a third input parameter. Such an analysis is presently being conducted. It is possible that the clean rain could have contributed to Zn dissolution if the amount of rain was strongly correlated to the $SO_4^=$ and NO_3^- depositions.

Laboratory studies show that the dry deposition of HCHO into dew enhances the dissolution of Zn, and $HCOO^-$ is produced in the dew. During the present exposure study, the dew was analyzed for $HCOO^-$ using ion chromatography; however, $HCOO^-$ in the dew does not appear to be stable and the results to date are qualitative. It appears that the dry deposition of HCHO may have contributed to the dissolution of Zn especially during the summer; however, the $HCOO^-$ data are not of sufficient quality to include in a regression analysis. Due to the inland position of the site, the dry and wet deposition of Cl^- was low and has not been included in the regression analysis.

Conclusions

The results of the field study show that wet deposition enhances the dissolution rate of Zn on galvanized steel and suggests that the enhancement is due to impurities such as $SO_4^=$ in the precipitation. Much of the Zn dissolved under both clean rain and dry deposition and total deposition conditions can be accounted for by dry and wet deposition of S species and their subsequent surface reactions with Zn compounds. The results of the two-parameter linear regression models are consistent with a model where each $SO_4^=$ molecule dissolves one Zn molecule.

The structure of the field data was such that the 90% confidence interval for the stoichiometric coefficient for NO_3^- included both 0 and 0.5, the value obtained from laboratory results, and therefore the data cannot be used to determine whether the deposition of NO_3^- influences corrosion. It does not appear, based on this preliminary analysis, that there is a substantial clean rain effect on the dissolution of Zn; however, more detailed statistical testing is required to determine whether such an offset exists. Substantial amounts of $HCOO^-$ were found in the runoff, but measured concentrations were not accurate enough to be included in the data analysis.

The results of this field study show that useful results can be obtained by conducting a controlled field study in which direct measurements of depositions of compounds are made, thereby eliminating the need to relate ambient concentrations to the amounts of compound deposited on a surface. However, the data generated from the study can only be used to test whether the data are consistent with the prediction models generated by other means because the environmental and meteorological conditions at the field site will rarely generate random variations of the amounts of depositions of potential corrosion-enhancing compounds such that the data set can be used to determine the relative contributions of each compound to the overall corrosion.

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TABLE 1. AVERAGE DRY AND TOTAL FLUXES[a]

	$F(Cl^-)$	% Dry	$F(NO_3^-)$	% Dry	$F(SO_4^{=})$	% Dry	F(Zn)	% Dry
Dry Deposition Plus Clean Rain	0.88	75	1.27	46	4.30	61	5.93	69
Total Deposition	1.18	–	2.75	–	7.10	–	8.55	–

[a]F(X) is the accumulated deposition of X divided by the exposure time in nmol/cm² day, and Dry % is the dry flux divided by the total flux.

TABLE 2. AVERAGES AND STANDARD DEVIATIONS OF AND CORRELATIONS BETWEEN INPUT AND OUTPUT VARIABLES[a]

	$x \pm \sigma_x$	$y \pm \sigma_y$	$z \pm \sigma_z$	r (x,y)	r (x,z)	r (y,z)
Dry Deposition Plus Clean Rain	21.57 ± 30.17	6.48 ± 8.06	30.72 ± 36.24	0.472	0.960	0.488
Total Deposition	36.34 ± 34.63	14.06 ± 12.92	43.90 ± 38.17	0.813	0.952	0.839

[a] $\bar{x}$ is the average value of x; σ_x is the standard deviation of x; and r(x,y) is the linear correlation coefficient between the variables x and y and is defined by the following expression:

$$r(x,y) = \frac{\frac{1}{N-1}\sum_{i=1}^{N}(x_i - \bar{x})(y_i - \bar{y})}{\sigma_x \sigma_y}$$

where x_i and y_i are the data points and N is equal to the number of data points.

TABLE 3. RESULTS OF TWO-PARAMETER LINEAR REGRESSION ANALYSES[a]

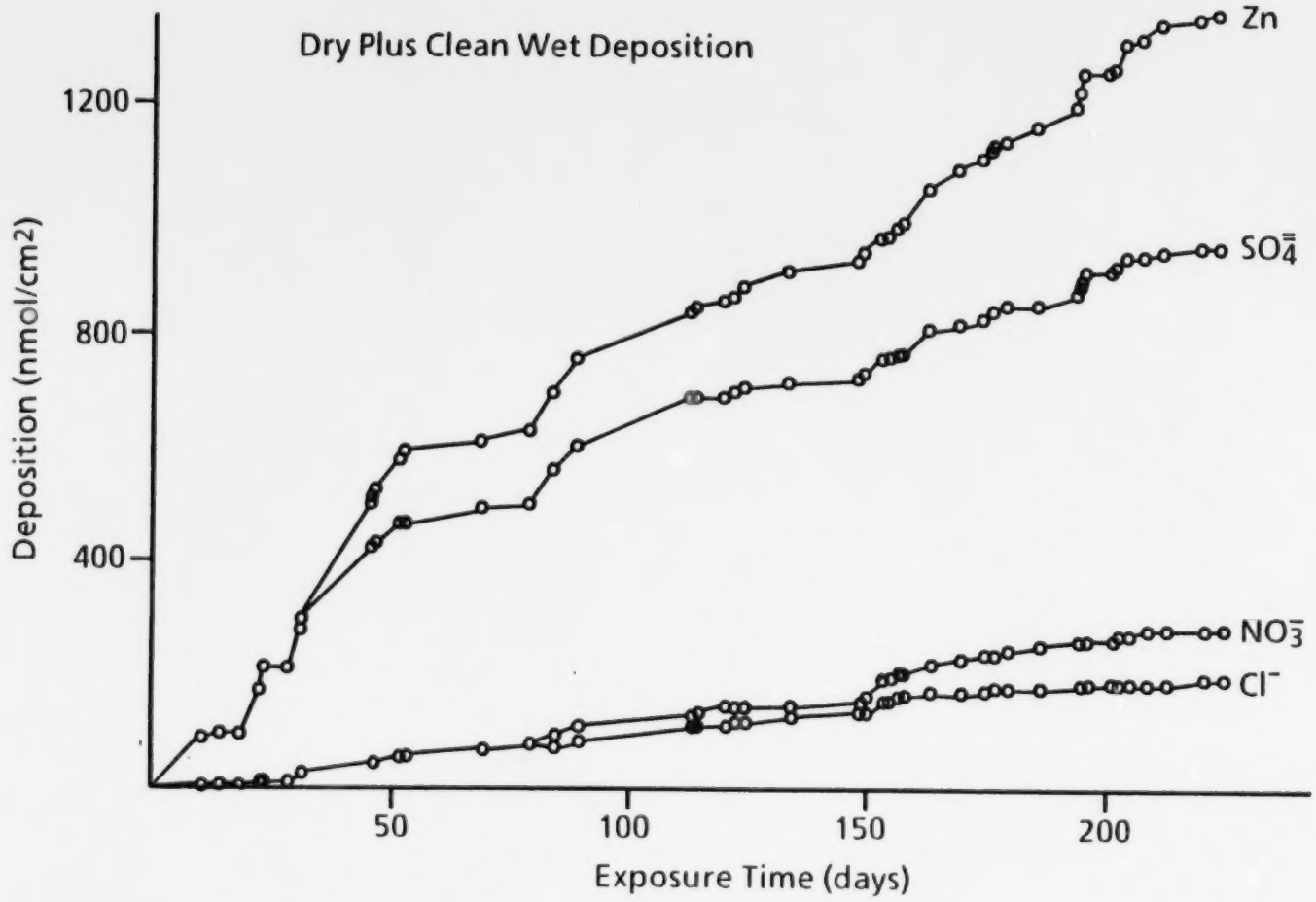
	$\alpha \pm SE(\alpha)$	$\beta \pm SE(\beta)$	$\phi \pm SE(\phi)$	R^2
Dry Deposition Plus Clean Rain	1.13 ± 0.07	0.20 ± 0.25	-4.94 ± 3.13	0.923
Total Deposition	0.88 ± 0.09	0.56 ± 0.24	6.19 ± 6.57	0.919

[a]SE(x) is the standard error in x, and R^2 is the multiple regression correlation coefficient.

TABLE 4. RESULTS OF ONE-PARAMETER LINEAR REGRESSION ANALYSES[a]

	$\alpha \pm SE(\alpha)$	$\phi \pm SE(\phi)$	R^2
Dry Deposition Plus Clean Rain	1.15 ± 0.06	-4.07 ± 2.21	0.922
Total Deposition	1.06 ± 0.06	7.55 ± 2.89	0.907

[a]See Table 3 for parameter definitions.


Dry Plus Clean Wet Deposition
Deposition (nmol/cm2)
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400
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100
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Exposure Time (days)
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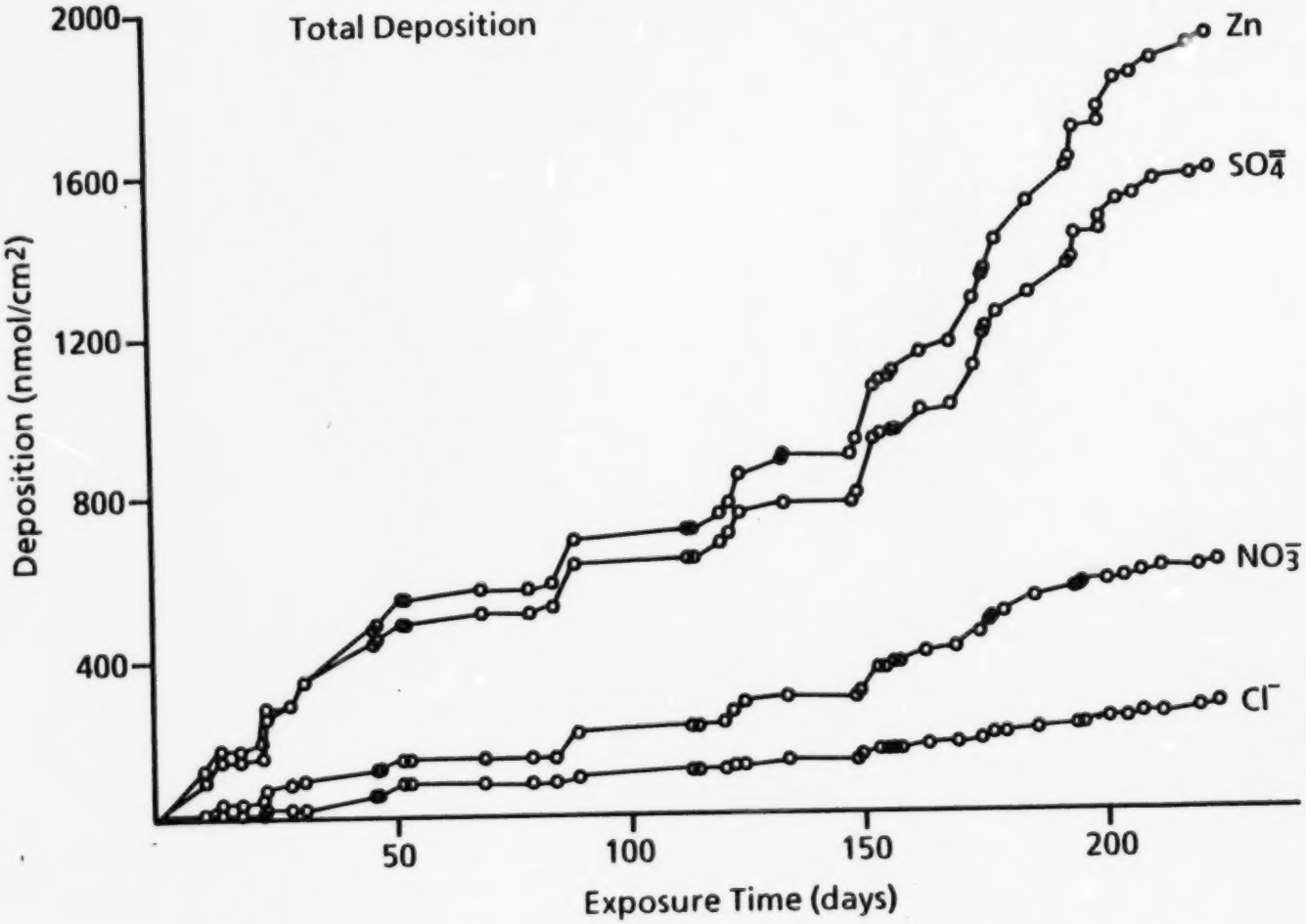
NO_3^{-}
Cl^{-}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Deposition (nmol/cm²)
2000
1600
1200
800
400
50
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150
200
Exposure Time (days)
Zn
$SO_4^{=}$
NO_3^{-}
Cl^{-}